X-ray Absorption Spectroscopy in the Physical and Biological Sciences

Bruce Ravel

Synchrotron Methods Group, Ceramics Division
National Institute of Standards and Technology

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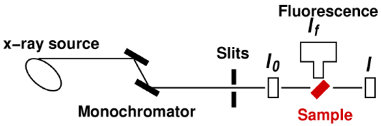
The XAS Experiment

An X-ray Absorption Spectroscopy experiment measures the probability as a function of energy that a material will absorb a photon in a given energy range.

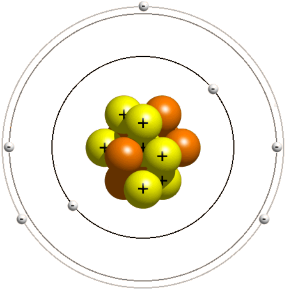
In its simplest form, an XAS beamline looks like this:



The monochromator uses Bragg diffraction to select the desired energy. The energy is scanned by changing the angle of the mono and the x-ray beam is directed from the mono to the sample.

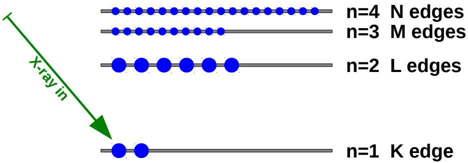
Model of the atom

All atoms are like little solar systems. Each element on the periodic table has a specific number of protons in the nucleus and electrons orbiting.



The electrons closer to the center are boudn with more energy than the higher lying electrons.

The basic physical process in XAS and XRF



1. An incoming photon interacts with a deep-core electron. Shown here, a 1s electron is excited for a K-edge spectrum.

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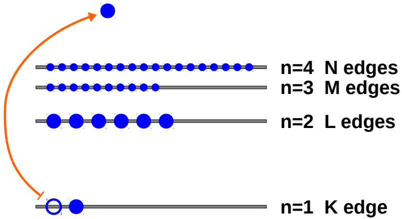

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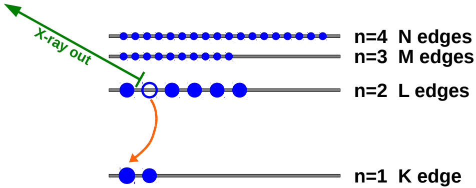

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2. The deep-core electron is promoted to some unoccupied state above the Fermi energy, propagates away, and leaves behind a core-hole.
3. A short time later (1 or 2 femtoseconds), a higher-lying electron decays into the core-hole and emits a photon.

Characteristic energies

Each element has a characteristic set of excitation and fluorescence energies. Two examples:

Iron: Z=26

Edge	Energy
K	7112
L3	706.8
L2	719.9
L1	844.6

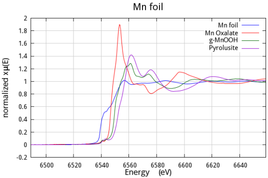
Line	Transition	Energy	Strength
Kα_1	K-L3	6405.2	0.580
Kα_2	K-L2	6392.1	0.294
Kβ_1	K-M3	7059.3	0.082
Kβ_3	K-M2	7059.3	0.043
Kβ_5	K-M4,5	7110.0	0.001

Uranium: Z=92

Edge	Energy
K	115606
L3	17166
L2	20948
L1	21757

Line	Transition	Energy	Strength
Lα_1	L3-M5	13614.0	0.686
Lα_2	L3-M4	13438.0	0.077
Lβ_2	L3-N4,5	16387.7	0.181
Lβ_5	L3-O4,5	17063.2	0.038
Lβ_6	L3-N1	15727.0	0.013
L$_\ell$	L3-M1	11618.0	0.005

Data Processing and Atomic Structure



- The absorption data show clear differences for Mn species of different valence. As the valence increases (Mn^0, Mn^{2+}, Mn^{3+}, Mn^{4+}), the edge position shifts to higher energy.

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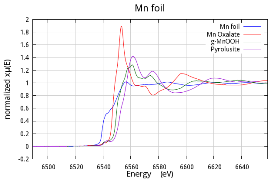

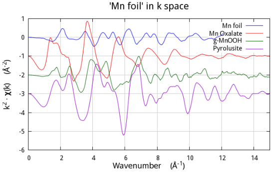

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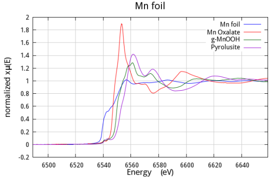
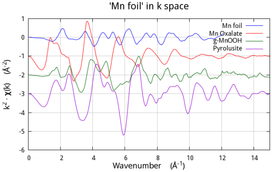
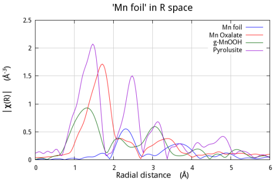






- The absorption data show clear differences for Mn species of different valence. As the valence increases (Mn^{0}, Mn^{2+}, Mn^{3+}, Mn^{4+}), the edge position shifts to higher energy.
- The oscillatory portion of the spectrum can be isolated and ...
- ... Fourier transformed. This FT function can be interpreted to yield a partial pair distribution functions of atoms about the absorber. The Mn-O distances are different for the Mn^{2+}, Mn^{3+}, and Mn^{4+} and clearly different from the Mn–Mn distance in Mn metal.

Information in the XAS Measurement

XAS is used to measure:

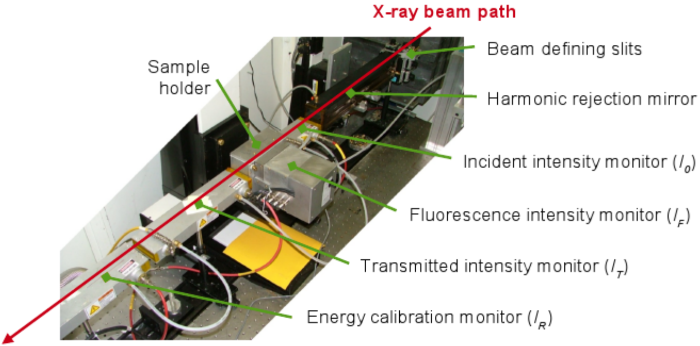
- The valence state of the absorbing atom independently of the chemistry of the rest of the sample
- The local configuration of atoms around the absorbing atom

XAS and Other Techniques

XAS is complementary to other synchrotron and laboratory measurements techniques, such as diffraction, NMR, electron miscroscopy, and many others.

Standard Hutch Instrumentation

Virtually every beamline provides a basic complement of detectors, optics, and sample positioners.

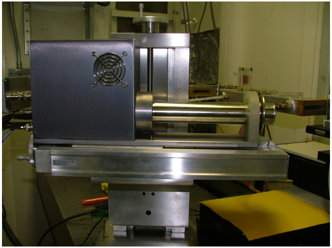


Transmission EXAFS: $\mu \cdot t = \ln(I_0 / I_T)$ (Beer's law)

Fluorescence EXAFS: $\mu \propto I_F / I_0$

Specialized Sample Environments

The fluorescence detector can be replaced with an energy discriminating detector which electronically isolates the desired signal.



This is particularly useful for sample with many components or with very low conctrations of the target element.

The sample holder can be replaced with:

- electrochemistry cell
- peristaltic fluid flow apparatus
- furnace
- cryostat
- magnet
- … and so on …

XAS Looks at Matter in All Forms

So ... why do an XAS experiment?

- XAS can be measured and interpreted with no assumption of symmetry or periodictity
- XAS is non-destructive
- X-rays penetrate deeply into the sample containment

XAS is used by researchers in a surprisingly broad array of scientific disciplines, such as:

- Catalysis and energy sciences
- Environmental sciences
- Materials science
- Organic and inorganic chemistry
- Life sciences
- and many others

Solving a real-world problem with XAFS

XANES as a fingerprinting technique

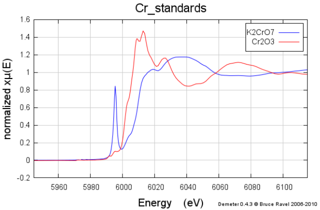
One of the most powerful uses of XANES data is to simply identify what is in front of the beam.

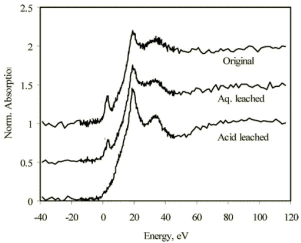
Highly toxic, water soluble Cr^{VI} can be distinguished from the non-toxic Cr^{III} form by simple examination of the near-edge spectra.

Here are spectra from coal ash as well as the residue after water and acid leaching experiments.

K_2CrO_7

Cr_2O_3



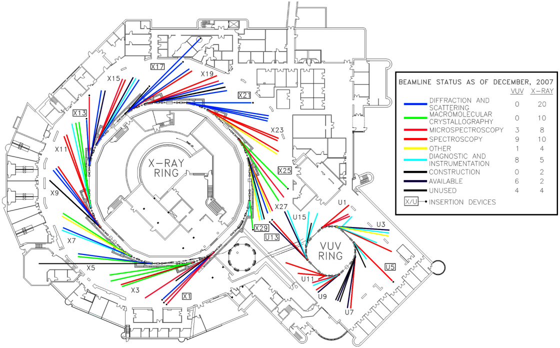


Quantifying Hazardous Species in Particulate Matter Derived from Fossil-Fuel Combustion, F.E. Huggins, et al., Environ. Sci. Technol. (2004) **38**:6, 1836 DOI: 10.1021/es0348748

XAS Beamlines at NSLS

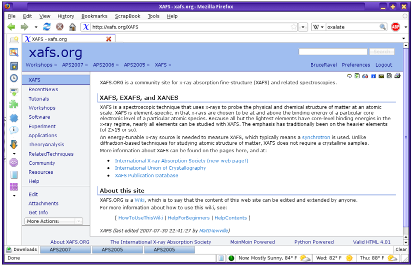
We have a comprehensive XAS program at NSLS – some highlights:

X3b	Biological applications
X18b	Time resolved XAS
X23a2	NIST + Industrial applications
X15b and X19a	“Tender” x-rays, including S, P, and Cl.
U7a and U4a	Soft x-rays, first row elements, transition metal L edges



The beamlines marked in red do XAS or a related inner shell spectroscopy.

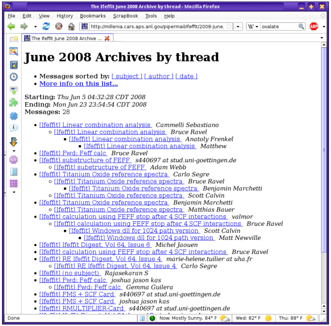
Internet Resources



http://xafs.org offers a growing volume of educational resources.

An earlier version of this talk has been posted on the Tutorials page.

> NSLS is developing web-based synchrotron education resources, starting with XAS!

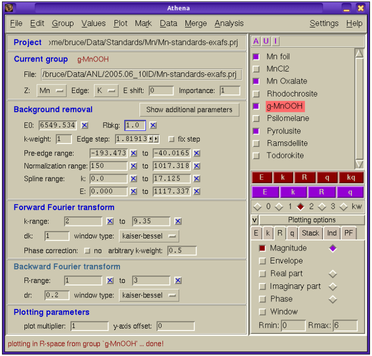


The IFEFFIT mailing list focuses on the analysis software package I co-author. It is a great place to ask questions about any aspect of XAS measurement, theory, or interpretation.

Analysis Software

The IFEFFIT package, written by Matt Newville (GSECARS, APS) and yours truly, is a thorough, high-quality XAS analysis solution. It is open source, free of cost, available on the web, always under development, fully supported, cross-platform, and in use by many hundreds of XAS practitioners worldwide.

ATHENA



HEPHAESTUS